REACNOSTICS

µ-DRIFTS

UNDERSTAND YOUR
CATALYST

OPTIMIZE YOUR
REACTOR

REACNOSTICS
Science & Engineering

REACNOSTICS µ-DRIFTS

The REACNOSTICS µ-DRIFTS optical accessory is tailored to fit most commercial FTIR-spectrometers and enables automated Diffusive Reflectance IR-Spectroscopy on solid catalyst samples coupled with accurate background subtraction and reference measurements.

Whether used as stand-alone operando spectroscopic cell for DRIFTS or coupled to one of REACNOSTICS spatial profile reactors for iso-potential DRIFTS, it enables the comprehensive investigation of bulk catalysts and surface adsorbates for a large variety of heterogeneous catalytic reactions at industrially relevant temperature and pressure conditions.

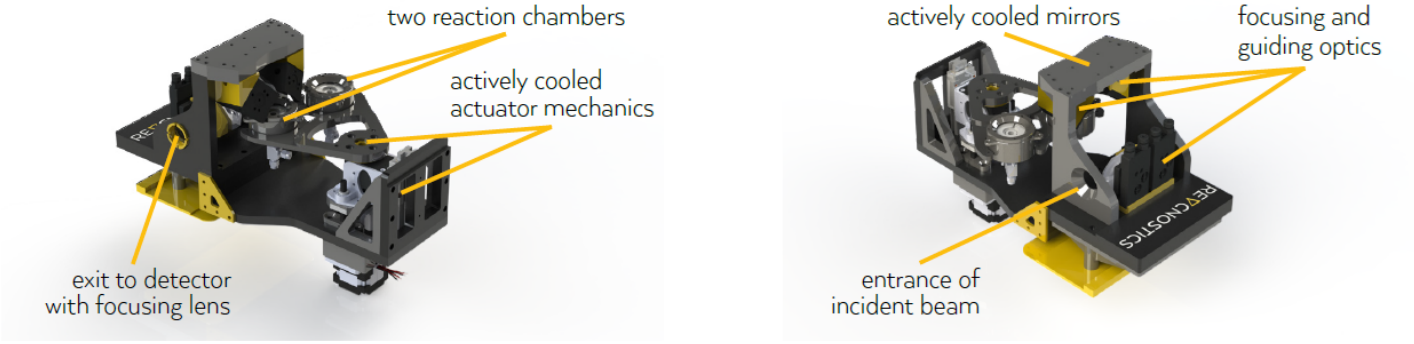


Figure 1: Front and back view of the µ-DRIFTS accessory

Paired with the REACNOSTICS Compact Profile Reactor (CPR) or any other catalytic reactor equipped with spatial sampling, µ-DRIFTS enables automated spatially resolved DRIFTS spectroscopy along an entire catalyst bed. The proprietary Iso-Potential Spectroscopy technique offered by REACNOSTICS enhances accuracy, precision and speed in operando-catalyst characterization. While the CPR delivers spatial concentration and temperature profiles along the catalyst bed with sub-millimeter resolution, µ-DRIFTS provides the corresponding profiles of surface adsorbates. Interpreting all of this information together allows establishing structure-activity correlations and verification or rejection of postulated reaction mechanisms.

Iso-potential spectroscopy in general and iso-potential DRIFTS in particular open up new possibilities in catalysis research by i) enabling to perform operando spectroscopy in realistic or even industrial catalytic reactors, ii) combining reactors which are optimized for the catalytic reaction with spectroscopic cells which are optimized for the respective spectroscopic method and iii) performing automatically operando-measurements under reaction conditions that really matter, viz. all conditions inside the catalytic reactor, from the inlet to the outlet.

µ-DRIFTS features two separate sample chambers. One sample chamber is filled with a sample of the pure catalyst for standard operando DRIFTS, or with a highly diluted catalyst sample for iso-potential DRIFTS. The other sample chamber is typically filled with a chemically inert reference material, e.g. the diluent, the catalyst support or a white standard. Each reaction chamber can be individually heated to temperatures up to 550 °C and can be pressurized up to 10 atm. Controlled heating of the IR-transparent window up to 200 °C prevents condensation of reaction components on the inner surface of the window leading to undesired and uncontrolled absorption of IR-radiation. Heating of all gas-ports and transfer lines prevents condensation of reactants or products along the flow path. Each sample chamber, the base plate and the focusing mirrors are water-cooled, avoiding heat input into temperature sensitive components such as gaskets, optical components or the spectrometer, even at maximum sample temperature.

By employing a high-precision actuator mechanism, each chamber can be put into the IR beam path facilitating automated spectra acquisition and referencing without the need for manual sample manipulation. If coupled with the CPR, sample chamber changes and reactor movement are synchronized allowing unattended profile measurements, e.g. overnight and during long-term measurement campaigns.

Robust adjustable mirror mounts, precise linear bearings and an elaborate design make µ-DRIFTS rigid and extraordinarily stable. µ-DRIFTS is equipped with 2 off-axis ellipsoidal mirrors focusing the IR beam onto the sample and collecting the diffusively scattered radiation which is then being focused by an additional focusing lens onto the detector. Specular reflected rays are almost completely eliminated by the fundamental optical design and fine tuning of all beam path mirrors. Only diffusely scattered IR-radiation from the sample reaches the detector.

As shown in Figure 2, µ-DRIFTS delivers a three times higher signal intensity than other DRIFTS accessories on the market resulting in a superior signal-to-noise ratio and allowing for sensitive detection of catalyst adsorbates, even when standard DGTS IR-detectors are being used. Interfering background signals such as absorptions by the gas phase above the catalyst or water and carbon dioxide in the beam path are effectively removed by subtraction of the reference channel. This results in spectra of exceptional quality allowing for the accurate identification of vibrational modes of surface adsorbates.

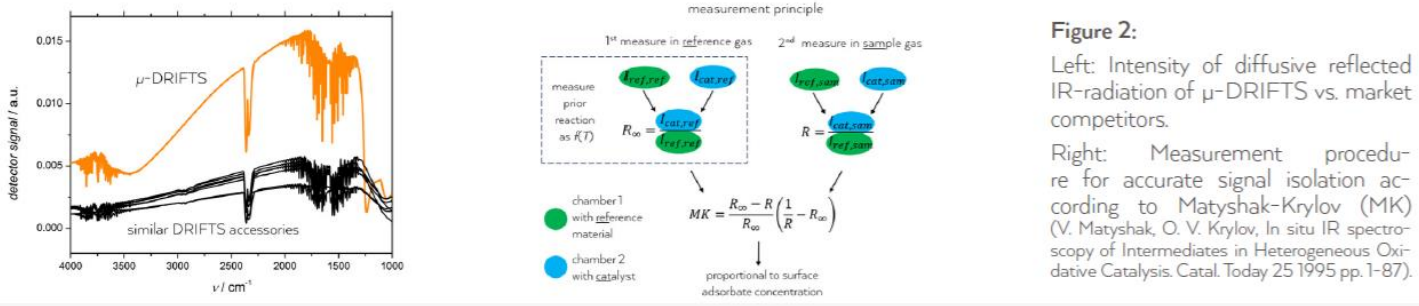


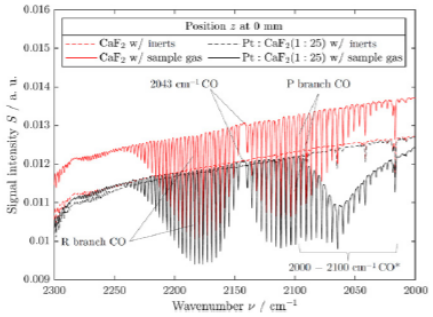
Figure 2:

Left: Intensity of diffusive reflected IR-radiation of µ-DRIFTS vs. market competitors.

Right: Measurement procedure for accurate signal isolation according to Matyshak-Krylov (MK) (V. Matyshak, O. V. Krylov, In situ IR spectroscopy of Intermediates in Heterogeneous Oxidative Catalysis. Catal. Today 25 1995 pp. 1-87).

To illustrate the principle of iso-potential DRIFTS and demonstrate the performance of µ-DRIFTS, the exothermic CO-oxidation ($CO + ½O_2 \rightarrow CO_2$ $\Delta H_r° = -283$ kJ/mol) on a $Pt/\gamma\text{-}Al_2O_3$ catalyst is shown in this application note as a simple test system.

A REACNOSTICS CPR was connected via iso-potential coupling with μ-DRIFTS sitting in a Bruker Vertex 70 IR-spectrometer to simultaneously measure molar flow rate-, temperature- and adsorbate profiles along the reactor. The Pt-nanoparticles were on average 2 nm in size, featuring some well-coordinated Pt-terrace sites (WC) and a majority of under-coordinated (UC) and highly under-coordinated (HUC) Pt-atoms at edges and corners of the Pt-nanoparticles respectively. The spectra presented in Figure 3 on the left side show single channel measurements conducted with the catalyst highly diluted in CaF_2 and the pure diluent CaF_2 under reference gas (He) and sample gas conditions. On the right side, the evaluated and isolated vibrational bands of CO adsorbed on the Pt-nanoparticles are depicted. The outstanding data quality facilitates the discrimination between different adsorption sites (e.g., well-coordinated, under-coordinated, and highly under-coordinated).



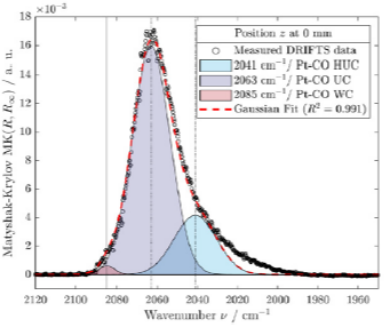


Figure 3:

Left: Single channel spectra of reference and sample measurements.

Right: Isolated absorption band of adsorbed CO together with a peak fit to deconvolute differently adsorbed CO molecules. Device: Bruker Vertex 70 @ 0.5 cm^{-1} and 64 scans.

Figure 4 shows the molar flow rate profiles and the temperature profile measured along the CPR. In the first 30 mm of the catalyst bed, the rate of CO oxidation to CO_2 is low and constant, leading to an almost linear decrease of CO and O_2 and a corresponding increase of CO_2. The reaction order of CO was determined to be -1 in this zone. Due to the significant heat release of the reaction, the catalyst temperature rises slowly but steadily. At around 31 mm, the reaction rate increases drastically. The reaction order with respect to CO changes rapidly from -1 to +1 as reflected by the exponentially decreasing CO flow rate.

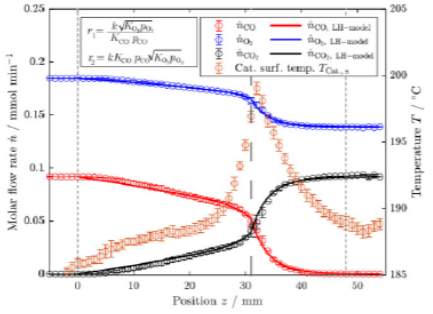


Figure 4:

Molar flow rate profiles, temperature profiles and kinetic fits obtained from the CPR. The catalyst bed is located in between the dashed lines.

The measured reactor profiles can be easily rationalized by correlating them with the corresponding DRIFTS spectra of adsorbed CO as shown in Figure 5. The slow and almost constant reaction rate in the first 30 mm of the catalyst bed is due to an almost complete coverage of the Pt-sites by CO. At low temperatures, CO binds strongly to Pt and very few Pt sites are accessible for O_2 adsorption, dissociation and eventually reaction. The effect of increasing reaction rate with decreasing CO concentration (reaction order -1) and decreasing O_2 concentration (reaction order +1/2) balance each other approximately out, leading to an almost constant reaction rate. At a certain threshold temperature, CO desorption increases and more Pt-sites become accessible for reaction, which leads to an acceleration of the reaction rate and a transition to the well known first order kinetics of CO oxidation on Pt.

Specifications

- designed for operando and iso-potential spectroscopy
- 3x higher signal intensity compared to other DRIFTS accessories on the market
- two individually controlled reaction chambers
- temperature measurement inside catalyst sample and reference sample
- temperature range: 50 °C to 550 °C
- pressure range: 1 atm to 10 atm
- spectral range: 1000 cm^{-1} to 5000 cm^{-1}
- heated window to avoid condensation problems
- minimized dead volume
- negligible blank activity of cell interior
- unprecedented mechanical and temperature stability
- precise optical alignment and focus
- automated and reproducible reaction chamber change
- software controlled heating & cooling
- automated spectra collection
- sample and reference under quasi-identical conditions
- no manual sample manipulation necessary
- full discrimination against specular reflection

A hotspot is formed in the catalyst bed with the temperature maximum being located at the maximum of the reaction rate (inflection point of the species profiles). CO is consumed rapidly in this second reaction zone. From about 40 mm on until the end of the catalyst bed at 55 mm the Pt surface is free of adsorbates as can be seen in the DRIFTS spectra.

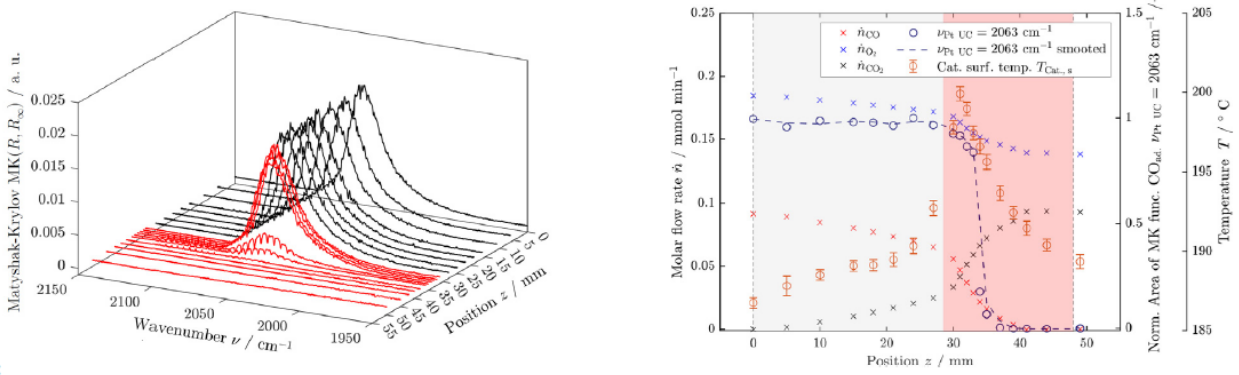


Figure 5:

Left: Spatially resolved vibrational bands of adsorbed CO on Pt.

Right: Gas phase concentration profile of CO oxidation together with the peak intensity of adsorbed CO and temperature by iso-potential DRIFTS.

While CO oxidation on Pt is mainly of academic interest and serves in this application note only as a simple demonstration reaction, it shows, how many catalytically important results iso-potential DRIFTS provides in a short time and the superior data quality of µ-DRIFTS.

If you would like to apply µ-DRIFTS to your own catalytic reaction, do not hesitate to contact REACNOSTICS (info@reacnostics.com). Knowing what is happening where and when in your reactor and on the catalyst surface will help you to optimize your catalytic process based on knowledge instead of trial and error.

Reacnostics GmbH
Am Kaiserkai 30
20457 Hamburg
Germany

REACNOSTICS
Science & Engineering

www.reacnostics.com